

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
3 May 2001 (03.05.2001)

PCT

(10) International Publication Number  
**WO 01/30949 A2**

- (51) International Patent Classification: **C11D**
- (21) International Application Number: PCT/US00/29295
- (22) International Filing Date: 23 October 2000 (23.10.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
9925472.4 28 October 1999 (28.10.1999) GB
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(81) Designated States (national): AE, AG, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KR (utility model), KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— Without international search report and to be republished upon receipt of that report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



**WO 01/30949 A2**

(54) Title: DETERGENT COMPOSITIONS

(57) Abstract: A detergent composition which dispenses and dissolves well in aqueous solution and having good storage stability is described. The composition comprises a reactive particle which preferably comprises first and second reactants which are respectively, acid and alkali-sources and which release gas on contact with water, in which the particle number ratio of the first reactant to the second reactant (that is the ratio of number of particles of the first reactant to the second reactant) in the reactive particle is at least 50:1. The reactive particles themselves are also claimed.

## Detergent Compositions

### 5 Field of the Invention

This invention relates to stable particulate components comprising two reactants which react with one another on contact with a fluid, in particular a liquid such as water, wherein such particles may be exposed to such fluid on storage, before the reaction is desired. The invention relates to providing such particulate components in a stable form,  
10 such that the reaction between the two reactants will substantially not take place until desired. The invention also relates to compositions containing such particulate components.

The invention particularly relates to effervescence particles which promote rapid dissolution for incorporation into compositions which need to dissolve readily and rapidly  
15 in an aqueous medium. The technology may find application in various fields such as cleaning compositions, in particular laundry and dishwashing detergent compositions which may be in a granular form or which may have been further processed into in a tablet form. The invention relates particularly to laundry detergent applications.

### Background of the Invention

20 Poor dissolution and dispensing problems are well-known in the detergent field. This problem has been exacerbated by recent tendencies to produce higher bulk density detergents, such as above 600g/l, to meet the consumer need for lower product and packaging volumes and less wastage i.e. higher active cleaning compositions. The problem is compounded by the use of detergent formulations which are based not on  
25 readily soluble phosphate builders, but instead on less soluble alternatives which overcome any environmental problems associated with phosphate builders. In addition, there is an increased need to promote rapid release of detergents into the wash water to provide greatest cleaning performance in short, energy-efficient wash cycles where the time of contact of the detergent solution with the items to be washed may be reduced to a  
30 minimum. Many solutions have been proposed to try to avoid the problems of poor dissolution and dispensing.

One such solution has been the use of effervescent systems in detergents. For example, detergent compositions comprising effervescing ingredients are described in WO98/04687. In WO98/04671, effervescence systems for use in detergents are disclosed in which in an effort to improve dissolution, acid and alkaline effervescing reactants

5 which react on contact with water to produce a gas, are mixed with a stabilising agent to produce a substantially anhydrous effervescence particle which has maximum efficacy on use in a washing step. Similarly, WO98/35011 also discloses particles comprising sodium bicarbonate and organic acid reactants which react together and which are formed into a particle with a binder. EP-A-918 087 describes co-builder particles for adding to  
10 detergent compositions, comprising bicarbonate and polycarboxylic acid which are formed by roller-compaction and which contain no free moisture. However, the requirements of providing good storage stability and good end use effervescence on contact with the wash liquor are conflicting requirements; the use of stabilising agents may prevent or reduce efficacy in the wash conditions, as the water contact with the  
15 effervescing reactants and the resulting reaction rate slows down, so that the effervescing and therefore, dissolution aid effect is undesirably reduced. There is therefore still a need for effervescence delivery systems for use in such applications which have good stability on storage and rapid dissolution and therefore release of effervescence, on contact with water on use.

#### 20 Summary of the Invention

The present inventors have found that surprisingly improved stability on storage and maximised efficacy on use can be achieved by careful selection of the particle sizes of the reactants in the effervescence particle.

Thus, in accordance with the present invention, there is provided a reactive  
25 particle comprising two particulate reactants which react together on contact with a reaction-promoting fluid, the particle number ratio of the first reactant to the second reactant (that is the ratio of number of particles of the first reactant to the second reactant) is at least 50:1. Preferably, the ratio of the median particle size of the second reactant to the first reactant is at least 2:1. Thus, although a larger number of the relatively larger  
30 particle size reactant may be used, preferably a larger number of the relatively smaller particle size reactant are used.

This combination of a large number of relatively smaller particle size reactant, and a smaller number of relatively larger particle size components has been found to lead to the surprising result that during a process for combining the first and second reactants to from the reactive particle, the larger particle size reactant acts as a "core" which is effectively surrounded in the reactive particle by the second component. Thus, the second component provides a barrier so that a fluid which promotes reaction between the two reactants cannot penetrate the barrier layer which acts as a barrier to moisture ingress to the interface between the two reactants, so that no reaction between the first and second reactants is promoted and storage stability is surprisingly, significantly improved.

In a preferred aspect of the invention, the particle is an effervescence particle in which at least one of each of the first and second reactants are respectively, an alkaline source and an acid source, and the fluid is a liquid i.e. water or other aqueous component. However, it will be clear to the skilled reader that the principle is more broadly applicable to improved stability of any other reactants where they may be exposed to a fluid (i.e. a liquid or a gas) which will promote their reaction with one another, prior to the desired in use conditions where exposure to the fluid is desirable.

The present invention also relates to detergent compositions comprising such effervescence particles.

The present invention also relates to washing processes in which a detergent composition comprising effervescence particles is contacted with water to provide rapid dissolution of the detergent composition in the water, and the water comprising dissolved detergent composition is then used for washing soiled articles. The invention is directed in particular to the washing of soiled household items, particularly dishwashing and/or laundry washing applications. The invention is particularly useful for laundry washing processes.

#### Detailed Description of the Invention

##### Reactive Particle

The reactive particle comprises two particulate reactants which react together on contact with a third component, generally a reaction-promoting fluid. The reaction-promoting fluid may be either a third reactant which is required for a reaction between the first and second reactants, or it may comprise a reaction medium either which enables penetration of a third reactant to the reactive particle so that a reaction takes place, or

which promotes contact between the first and second reactants so that the reaction between the first and second components is enabled or promoted. The invention is particularly useful where the fluid is a liquid and in particular where the fluid is water, which may come into contact with the reactive particle either in the gaseous or liquid phase. In particular the reactive particle may comprise an effervescence particle where the first and second reactants react with one another on contact with water to produce effervescence. Thus, in this embodiment, at least one of each of the first and second reactants comprises an acid source and at least one comprises an alkali source.

The particle number ratio of the first reactant to the second reactant (that is the ratio of number of particles of the first reactant to the second reactant) is at least 50:1, preferably at least 100:1, more preferably at least 500:1, or even at least 1000:1 and most preferably at least 5000:1 or even at least 10000:1.

In addition, the ratio of the median particle size of the second reactant to the first reactant is at least 2:1, preferably at least 8:1, more preferably at least 15:1, or at least 20:1 or even at least 30:1. Preferably the span of the particle size of each reactant is no greater than 3, more preferably no greater than 2, most preferably no greater than 1.5.

As used herein, the phrase "median particle size" means the geometric mass median diameter of a set of discrete particles as measured by any standard mass-based particle size measurement technique, preferably by dry sieving. As used herein, the phrase "geometric standard deviation" or "span" of a particle size distribution means the geometric breadth of the best-fitted log-normal function to the above-mentioned particle size data which can be accomplished by the ratio of the diameter of the 84.13 percentile divided by the diameter of the 50<sup>th</sup> percentile of the cumulative distribution ( $D_{84.13}/D_{50}$ ). See Gotoh et al, *Powder Technology Handbook*, pp. 6-11, Marcel Dekker 1997.

Preferably, the mean particle size of the particles is from about 500 microns to about 1500 microns, more preferably from about 600 microns to about 1200 microns, and most preferably from about 700 microns to about 1000 microns. The particle size distribution is defined by a relatively tight geometric standard deviation or "span" so as not to have too many particles outside of the target size. Accordingly, the geometric standard deviation is preferably is from about 1 to about 2, more preferably is from about 1.0 to about 1.7, even more preferably is from about 1.0 to about 1.4, and most preferably is from about 1.0 to about 1.2.

In particular for preparing an effervescence particle to be used for example, in a household or industrial cleaning application, the median particle size of the second reactant is preferably greater than 100 $\mu$ m, more preferably greater than 200 $\mu$ m and most preferably greater than 300 $\mu$ m. The particle size of the first reactant is preferably below 50 $\mu$ m, more preferably below 25 $\mu$ m and most preferably below 10 $\mu$ m. Where the reactive particle is an effervescence particle, the first reactant comprises either the acid source or the alkali source, but preferably comprises the alkali source, and the second reactant preferably comprises acid source.

The first reactant is preferably present in the reactive particles at a level of from 0.1% to 99% by weight of the total particle, preferably from 3% to 80%, more preferably from 10% to 75% and most preferably from 15% to 70%.

The second reactant is preferably present in the reactive particles at a level of from 0.1% to 99% by weight of the total, preferably from 20% to 95%, more preferably from 30% to 85% and most preferably from 35% to 75% by weight of the effervescence particle. For optimum reaction, the weight ratio of the first and second reactants, in the reactive particle is preferably substantially stoichiometric, such that there are substantially equal moles of reactive groups. Thus, the moles of reactive group of first reactant to second reactant are preferably from 5:1 to 1:5, more preferably from 3:1 to 1:3, more preferably from 3:2 to 2:3 and most preferably from 9:10 to 10:9.

Suitable acid sources include solid organic, mineral or inorganic acids, salts or derivatives thereof or mixtures thereof. It may be preferred that the acids are mono-, bi- or tri-protonic acids. Such acids include mono- or polycarboxylic acids preferably citric acid, adipic acid, glutaric acid, 3-chetoglutaric acid, citramalic acid, tartaric acid, maleic acid, fumaric acid, malic acid, succinic acid, malonic acid. Such acids are preferably used in their acidic form. Derivatives also include esters of the acids. Preferred acids include citric acid and malic acid. Citric acid is particularly preferred.

Any alkali-source may be used in the reactive particle. Carbonate alkali-sources are particularly preferred, for example including carbonate, bicarbonate, sesquicarbonate and percarbonate salts, in particular bicarbonate and/or carbonate. Preferred carbonates to be used herein include carbonate and hydrogen carbonates which should be present in the effervescence particle in a form which can react with the acid-source. Generally, therefore, the alkali-source should be water soluble, or of very fine particle size such that

a reaction with the acid-source takes place readily on contact of the effervescence particle with water. Salts of alkali metals or alkaline earth metals are suitable. Water-soluble salts such as salts of potassium, lithium, sodium, and the like are preferred amongst which sodium and potassium carbonate are particularly preferred. Suitable bicarbonates to be  
5 used herein include any alkali metal salt of bicarbonate like lithium, sodium, potassium and the like, amongst which sodium and potassium bicarbonate are preferred. Bicarbonate may be preferred to carbonate, because it is more-weight effective, i.e., at parity weight bicarbonate is a larger CO<sub>2</sub> "reservoir" than carbonate. However, overall detergent formulation requirements may result in the more alkaline pH, produced by  
10 carbonates, providing a more useful overall detergent formulation, thus the choice of carbonate or bicarbonate or mixtures thereof in the effervescence granules may depend on the pH desired in the aqueous medium wherein the detergent composition comprising the effervescence particles is dissolved. For example where a relatively high pH is desired in the aqueous medium (e.g., above pH 9.5) it may be preferred to use carbonate alone or to  
15 use a combination of carbonate and bicarbonate wherein the level of carbonate is higher than the level of bicarbonate, typically in a weight ratio of carbonate to bicarbonate from 0.1 to 10, more preferably from 1 to 5 and most preferably from 1 to 2. In one aspect of the invention, where the detergent composition comprises bicarbonate alone as the alkali-source, preferably the effervescence particle additionally comprises greater than 6 wt%  
20 citric acid optionally in mixtures with other acid-source components.

Preferably the reactant particle, is substantially anhydrous such that the overall moisture content (including both bound i.e. water of crystallisation, and unbound i.e. free moisture) is less than 0.5 wt% of the effervescence particle. This is particularly preferred where the reaction-promoting fluid is water, or where water promotes contact of the  
25 reaction-promoting fluid with the reactants. More particularly, where the effervescence particle comprises both acid-source and alkali-source, preferably at least the acid-source used for forming the effervescence particle has an overall moisture content less than 0.1 wt%, more preferably less than 0.05 wt% and most preferably less than 0.01 wt%. More preferably, the alkali-source also has an overall moisture content less than 0.1 wt% ,  
30 more preferably less than 0.05 wt% and most preferably less than 0.01 wt%.

Preferably, the effervescence particles have a particle size such that the median particle size is from 0.001 mm to 7 mm, preferably less than 2 mm.

The bulk density of the effervescence particles is preferably from 500 g/l to 1200 g/l, more preferably from 700 g/l to 1100 g/l.

The reactive particles may optionally comprise additional ingredients. Generally, the effervescence particles comprise no more than 50 wt% of the particle of additional  
5 ingredient(s), preferably no more than 35 wt% and more preferably no more than 20% or 10%. It may be particularly preferred to have a highly active particle comprising no more than 5 wt% or even no more than 2 wt% of additional ingredients besides the components which contribute to the gas production/release. Where the reactive particle is an effervescence particle for use in a detergent composition, suitable additional ingredients  
10 may comprise any of the detergent ingredients which are described below simply or in mixtures. Particularly suitable are surfactants or organic or inorganic builder components, preferably those which are water soluble such as those described below.

The reactive particles of the invention may optionally comprise binders or coatings. Suitable bonding or coating materials are selected from one or mixtures of  
15 more than one of the binders and coating materials known to those skilled in the art. In particular suitable binders include anionic surfactants like C6-C20 alkyl or alkylaryl sulphonates or sulphates, preferably C8-C20 alkylbenzene sulphonates, cellulose derivatives such as carboxymethylcellulose and homo- or co- polymeric polycarboxylic acid or their salts, nonionic surfactants, preferably C10-C20 alcohol ethoxylates  
20 containing from 5-100 moles of ethylene oxide per mole of alcohol and more preferably the C15-C20 primary alcohol ethoxylates containing from 20-100 moles of ethylene oxide per mole of alcohol. Of these tallow alcohol ethoxylated with 25 moles of ethylene oxide per mole of alcohol (TAE25) or 50 moles of ethylene oxide per mole of alcohol (TAE50) are preferred. Other preferred binders include the polymeric materials like  
25 polyvinylpyrrolidones with an average molecular weight of from 12 000 to 700 000 and polyethylene glycols with an average weight of from 600 to 10 000. Copolymers of maleic anhydride with ethylene, methylvinyl ether, methacrylic acid or acrylic acid are other examples of polymeric binders. Others binders further include C10-C20 mono and diglycerol ethers as well as C10-C20 fatty acids. In the embodiment of the present  
30 invention where a binder is desired C8-C20 alkylbenzene sulphonates are particularly preferred.



The reactive particles used in the present invention are preferably prepared by mixing the reactant component(s) with any additional ingredients to produce an intimate mixture and then submitting the mixture to a granulation step to form particles. Any granulation process may be used, however, in order to maintain high active levels in the finished reactive particles, the granulation should preferably take place substantially without addition of any free moisture to the mixture. Conventional agglomeration, extrusion, marumerisation, compaction processes are all suitable. However, a preferred agglomeration step comprises a pressure agglomeration step to form an agglomerate mixture, followed if necessary by a granulation step in which the agglomerate is formed into the reactive particles, such as effervescence particles for use in the detergent compositions of the invention.

In the preferred pressure agglomeration process, the substantially dry mixture comprising the reactants and any optional additional ingredients is exposed to high external forces that bring the particles closely together thereby densifying the bulk mass of said particles and creating binding mechanisms between the components in the mixture. Indeed, pressure agglomeration results in an aggregation mechanism which is characterised by the presence of inter-particle bonds between primary solid effervescent particles and a structure in which these effervescence particles are still identifiable and retain many of their characteristics, e.g. the ability to react together in presence of water to deliver carbon dioxide.

The increase of density associated with the preferred processes for making the reactive particles for use in the present invention, is closely linked to the pressure applied. Typically, the bulk density will increase up to 200g/l, preferably from 10 g/l to 150 g/l, starting from the density of the mixture comprising the effervescent raw materials, i.e., acid and the carbonate source, and optionally the binder, before having undergone a pressure agglomeration.

Pressure agglomeration may be carried out using different processes which can be classified by the level of forces applied. A preferred process to be used herein is roller compaction. In this process the reactants, preferably the acid-source and the alkali-source and any optional additional ingredients after having been mixed together are forced between two compaction rolls that applies a pressure to said mixture so that the rotation

of the rolls transforms the mixture into a compacted sheet/flake. This compacted sheet/flake is then broken up to form reactive i.e. effervescence particles.

Typical roller compactors for use herein are for example Pharmapaktor L200/50P® commercially available from Hosokawa Bepex GmbH. The process variables during the pressure agglomeration step via roller compaction are the distance between the rolls, the feed rate, the compaction pressure and the roll speed. A typical feeding device is a feed screw. The distance between the rolls is typically from 0.5 cm to 10 cm, preferably from 3 to 7 cm, more preferably from 4 to 6 cm. The pressing force is typically between 20 kN and 120 kN, preferably from 30 kN to 100kN, more preferably from 50 kN to 100 kN. Typically, the roll speed is between 1 rpm and 180 rpm, preferably from 2 rpm to 50 rpm and more preferably from 2 rpm to 35 rpm. Typically, the feed rate is between 1 rpm and 100 rpm, preferably from 5 rpm to 70 rpm, more preferably from 8 rpm to 50 rpm. Temperature at which compaction is carried out is not critical, typically it varies from 0° C to 40 °C.

The sheet/flake produced by the pressure agglomeration process is broken up into effervescence particles by any suitable method for reducing the size of the sheet/flake to form particles, for example, by cutting, chopping or breaking the sheet/flake to produce the required length, and if necessary, by a process to make the particles rounded i.e. to obtain round or spherical granules according to the diameter size as defined herein before. In the preferred embodiment one way to break up the sheet/flake after the roller compaction step is to mill the compacted flake/sheet. Milling may typically be carried out with a Flake Crusher FC 200® commercially available from Hosokawa Bepex GmbH.

Depending on the particle size required for the effervescence particles, the milled material may be sieved further. Such a sieving of the effervescence granules can be carried out, for example with a commercially available Alpine Airjet Screen®.

In a preferred process for preparing a reactive particle in which water is a reaction-promoting fluid, processing takes place under controlled conditions to minimise the amount of moisture which can contact the respective reactants as they are formed into a reactive particle. The inventors have found that even trace amounts of moisture can adversely affect the stability of the reactive particle produced. In particular, where the reaction is between the first and second reactants is a self-accelerating reaction, for example where the reaction between the two reactants produces water as a by-product,

this may be particularly important. One particular example of where this factor is important is where the particle being produced is an effervescence particle which is formed from two reactants which are respectively, acid source and alkali-source, in particular such as organic acids (e.g. citric acid) and a carbonate source, respectively.

5           Thus, in such a preferred process, the first and second reactants are formed into a reactive particle such as an effervescence particle in over-dried conditions, in which atmospheric moisture is reduced from the processing environment. Generally this is achieved by the use of a dehumidifier. Preferably, the Relative Humidity (RH) is less than 40%, more preferably less than 30% and most preferably less than 20%. Preferably,  
10 in addition, at least one and preferably both of the reactants as provided in an over-dried form for preparing into the reactive particles of the invention. By "over-dried" is meant that the reactant is provided in a form which is both dry (i.e. substantially all of the free moisture is removed) and in addition, is at least partially anhydrous (so that at least some of the bound water, such as water of crystallisation or other water bound to the structure  
15 of the reactant, has been removed). Thus, preferably, when the first and second reactants contact one another preferably one, and more preferably both reactants have an overall moisture content (comprising both free and water of crystallisation which can be measured to drying at 120°C for 2 hours in a drying oven) is no greater than 0-1% by weight, more preferably no greater than 0.05% by weight and most preferably no greater  
20 than 0.01%.

#### Detergent Compositions Comprising an Effervescence Particle

In accordance with the present invention, there is also provided a detergent composition comprising a detergent matrix and the effervescence particle described above. The detergent matrix may be any conventional detergent composition. Generally,  
25 however, it comprises a pre-formed detergent matrix component comprising surfactant, and optional additional detergent ingredients. Preferably on contact of the effervescence particle, the eRH of the matrix will be no greater than 25%, more preferably no greater than 20% or even no greater than 15% or 12% or even 10%. The eRH is measured using a Rotronic™ Hygroskop DT calibrated according to the manufacturers instructions as set  
30 out in the Rotronic Hygroskop application leaflet 2/E Spi/S dated 3.1.83, using defined saturated salt solutions which cover the humidity range to be tested. All measurements are taken at 25°C.

In a preferred aspect of the invention, at least one of the components in the detergent matrix is over-dried i.e. has been dried to a level such that water which is bound to one or more of the detergent ingredients either in the detergent matrix component or optional additional detergent ingredients, is removed.

5 Detergent Matrix Component

The detergent matrix generally comprises a detergent matrix component. Such component comprises a pre-formed particulate which may be in the form of a powder, particle, flake or other solid form, comprising surfactant and optional additional detergent ingredients.

10 The surfactant may be anionic, nonionic, cationic, amphoteric, zwitterionic or mixtures thereof. Preferred detergent matrix components comprise anionic, nonionic and/or cationic surfactants. In particular matrix components which comprise anionic surfactant may be particularly useful. Suitable surfactants are described in more detail below. The surfactant content of a pre-formed matrix component is preferably from 5 to  
15 80 % by weight of the matrix component. Amounts of surfactants above 10 or even above 30% may be preferred. Amounts of surfactant below 70% or even below 50% may be preferred.

The detergent matrix component generally also contains a solid material which may be filler such as sulphates, in particular sodium sulphate, but more preferably  
20 comprises at least one detergent ingredient, in particular, builder or alkalinity components, or mixtures of such components. Suitable examples include phosphate, aluminosilicate, crystalline layered silicates, sodium carbonate or amorphous silicates. These materials are described below in more detail. For example, each of these components individually, or in mixtures may be present in amounts above 5%, preferably  
25 above 10% or even above 20% by weight of the content of the pre-formed matrix component. Particularly preferred builder components are sodium carbonate and/or zeolite. Zeolite A and zeolite MAP are both suitable.

A pre-formed matrix component preferably also comprises an organic builder such as a poly carboxylic acid and/or salt such as citric acid, tartaric acid, malic acid,  
30 succinic acid and their salts or a polymeric polycarboxylate such as polymers based on acrylic acids or maleic acids or co-polymers thereof. Such components are generally

present in the matrix component at levels below 15 wt %, preferably below 10 wt % of the matrix component.

Other preferred ingredients in the pre-formed matrix component are chelants such as phosphonate chelants NTA, DTPA and succinic acid derivative chelants, as described  
5 below. These components are preferably present in a pre-formed particulate component in amounts below 5 wt % or even below 2 wt % of the matrix component.

The detergent matrix may comprise one or more pre-formed detergent matrix components. Suitable pre-formed components may have been formed by spray-drying, agglomeration, marumerisation, extrusion or compaction, all of which methods for  
10 combining detergent ingredients are well-known in the art. Particularly preferred pre-formed matrix components are powders obtained from spray-drying processes, agglomerates and extrudates. Spray-dried powders are particularly useful. Detergent matrix components made according to at least one low shear mixing step, for example in a fluidised bed, for example by fluid bed agglomeration are also preferred.

15 Suitable spray-drying processes for forming such pre-formed detergent matrix components are described for example in EP-A-763594 or EP-A-437888. Suitable processes for forming detergent matrix components which are agglomerates are described for example in WO93/25378, EP-A-367339, EP-A-420317 or EP-A-506184. Suitable moderate to low shear mixers may be for example a Lodige KM (trademark)  
20 (Ploughshare) moderate speed mixer, or mixer made by Fukae, Draes, Schugi or similar brand mixers which mix with only moderate to low shear. The Lodige KM (ploughshare) moderate speed mixer which is a preferred mixer for use in the present invention comprises a horizontal hollow static cylinder having a centrally mounted rotating shaft around which several plough-shaped blades are attached. Preferably, the shaft rotates at a  
25 speed of from about 15 rpm to about 140 rpm, more preferably from about 80 rpm to about 120 rpm. The grinding or pulverizing is accomplished by cutters, generally smaller in size than the rotating shaft, which preferably operate at about 3600 rpm. Other mixers similar in nature which are suitable for use in the process include the Lodige Ploughshare  
30 <sup>TM</sup> mixer and the Draes® K-T 160 mixer. Generally, in the processes of the present invention, the shear will be no greater than the shear produced by a Lodige KM mixer with the tip speed of the ploughs below 10 m/s, or even below 8m/s or even lower.

Preferably, the mean residence time of the various starting detergent ingredients in the low or moderate speed mixer is preferably in range from about 0.1 minutes to about 15 minutes, most preferably the residence time is about 0.5 to about 5 minutes. In this way, the density of the resulting detergent agglomerates is at the desired level.

5 Other suitable mixers for use in the present invention are low or very low shear mixers such as rotating bowl agglomerators, drum agglomerators, pan agglomerators and fluid bed agglomerators.

Fluid bed agglomerators are particularly preferred. Typical fluidised bed agglomerators are operated at a superficial air velocity of from 0.4 to 4 m/s, either under  
10 positive or negative pressure. Inlet air temperatures generally range from -10 or 5°C up to 250°C. However inlet air temperatures are generally below 200°C, or even below 150°C. Suitable processes are described for example in WO98/58046 or WO99/03964. Suitable processes for forming detergent matrix components by extrusion are described for example in WO91/02047.

15 The detergent matrix may comprise only one pre-formed component as described or it may comprise a mixture of components, for example mixtures of different spray dried powders or of different agglomerates etc or mixtures of combinations of agglomerates, spray dried powders and/or extrudates etc. as described above.

Particularly preferred detergent matrix components are spray dried powders.

#### 20 Additional Detergent Ingredients

As described above, the detergent matrix will comprise surfactant and may comprise one or more additional detergent ingredients. These may comprise detergent raw materials or may be pre-formed particulates made by processing at least one detergent ingredient with other ingredients which may be active or inactive in the  
25 detergent, to form a solid particulate. Where the particulate components are detergent raw materials, any particulate detergent ingredient is suitable. These may be solid surfactants or soaps, or water soluble or dispersible polymeric materials, enzymes, bleaching components such as bleach activators or bleach salts such as peroxy salts. Surfactants and additional detergent ingredients are discussed in more detail below.

30 Any of the ingredients listed below may be added either as individual solid particulates or as pre-formed particulates or via the detergent matrix component. These additional

detergent ingredients must be incorporated into the detergent matrix if needed, having undergone a drying step. The final detergent matrix preferably has an eRH below 30%.

#### Detergent Ingredients

##### Surfactant

5           Suitable surfactants for use in the invention are anionic, nonionic, ampholytic, and zwitterionic classes of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

10           Preferably, the detergent compositions of the present invention and compositions comprising such particles comprises an additional anionic surfactant. Essentially any anionic surfactants useful for deterative purposes can be comprised in the detergent composition. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine  
15       salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate and sulfonate surfactants are preferred.

          The anionic surfactants may be present in the detergent matrix component in amounts below 25 wt % or even below 20 wt % but in a final detergent composition comprising the particle, is preferably present at a level of from 0.1% to 60%, more  
20       preferably from 1 to 40%, most preferably from 5% to 30% by weight.

          Other anionic surfactants include the anionic carboxylate surfactants such as alkyl ethoxy carboxylates, alkyl polyethoxy polycarboxylates and soaps ("alkyl carboxyls") such as water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid,  
25       2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors. Other suitable anionic surfactants are the alkali metal sarcosinates of formula  $R-CON(R^1)CH_2COOM$ , wherein R is a  $C_5-C_{17}$  linear or branched alkyl or alkenyl group,  $R^1$  is a  $C_1-C_4$  alkyl group and M is an alkali metal ion. Other anionic surfactants include isethionates such as the acyl isethionates, N-acyl  
30       taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfo succinates, monoesters of sulfosuccinate (especially saturated and unsaturated  $C_{12}-C_{18}$  monoesters)

diesters of sulfosuccinate (especially saturated and unsaturated C<sub>6</sub>-C<sub>14</sub> diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

5        Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C<sub>5</sub>-C<sub>17</sub> acyl-N-(C<sub>1</sub>-C<sub>4</sub> alkyl) and -N-(C<sub>1</sub>-C<sub>2</sub> hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described  
10        herein). Alkyl sulfate surfactants are preferably selected from the linear and branched primary C<sub>10</sub>-C<sub>18</sub> alkyl sulfates, more preferably the C<sub>11</sub>-C<sub>15</sub> branched chain alkyl sulfates and the C<sub>12</sub>-C<sub>14</sub> linear chain alkyl sulfates. Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C<sub>10</sub>-C<sub>18</sub> alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More  
15        preferably, the alkyl ethoxysulfate surfactant is a C<sub>11</sub>-C<sub>18</sub>, most preferably C<sub>11</sub>-C<sub>15</sub> alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

Preferred surfactant combinations are mixtures of the preferred alkyl sulfate and/or sulfonate and alkyl ethoxysulfate surfactants optionally with cationic surfactant. Such  
20        mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic sulfonate surfactants suitable for use herein include the salts of C<sub>5</sub>-C<sub>20</sub> linear alkylbenzene sulfonates, alkyl ester sulfonates, C<sub>6</sub>-C<sub>22</sub> primary or secondary alkane sulfonates, C<sub>6</sub>-C<sub>24</sub> olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any  
25        mixtures thereof.

Essentially any alkoxylated nonionic surfactant or mixture is suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

Preferred alkoxylated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic  
30        ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates



with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are particularly  
 5 suitable for use herein. Particularly preferred are the condensation products of straight or branched, primary or secondary alcohols having an alkyl group containing from 6 to 22 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula  $R^2CONR^1Z$  wherein:  $R^1$  is H,  $C_1$ - $C_4$  hydrocarbyl, 2-hydroxy ethyl,  
 10 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable  $C_1$ - $C_4$  alkyl; and  $R^2$  is a  $C_5$ - $C_{31}$  hydrocarbyl; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent  
 15 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units. Preferred alkylpolyglycosides have the formula:



wherein  $R^2$  is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

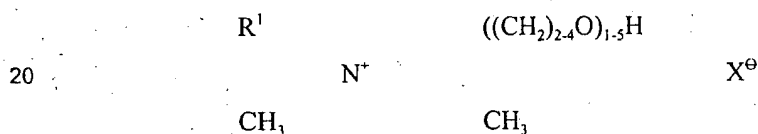
Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids. Suitable amine oxides include those compounds  
 25 having the formula  $R^3(OR^4)_xN^0(R^5)_2$  wherein  $R^3$  is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms;  $R^4$  is an alkylene or hydroxyalkylene group containing from  
 30 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and

each R<sup>5</sup> is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C<sub>10</sub>-C<sub>18</sub> alkyl dimethylamine oxide, and C<sub>10-18</sub> acylamido alkyl dimethylamine oxide.

Zwitterionic surfactants can also be incorporated into the detergent compositions in accord with the invention. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaines such as C<sub>12-18</sub> dimethyl-ammonio hexanoate and the C<sub>10-18</sub> acylamidopropane (or ethane) dimethyl (or diethyl) betaines and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Suitable cationic surfactants to be used herein include the quaternary ammonium surfactants. Preferably the quaternary ammonium surfactant is a mono C<sub>6</sub>-C<sub>16</sub>, preferably C<sub>6</sub>-C<sub>10</sub> N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups. Preferred are also the mono-alkoxylated and bis-alkoxylated amine surfactants.

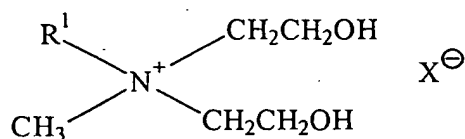
Cationic ester surfactants such as choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529 are also suitable as are cationic mono-alkoxylated amine surfactants preferably of the general formula I:



wherein R<sup>1</sup> is C<sub>10</sub>-C<sub>18</sub> hydrocarbyl and mixtures thereof, especially C<sub>10</sub>-C<sub>14</sub> alkyl, preferably C<sub>10</sub> and C<sub>12</sub> alkyl, and X is any convenient anion to provide charge balance, preferably chloride or bromide.

The levels of the cationic mono-alkoxylated amine surfactants in the detergent compositions of the invention are generally from 0.1% to 20%, preferably from 0.2% to 7%, most preferably from 0.3% to 3.0% by weight.

Cationic bis-alkoxylated amine surfactant such as



are also useful, wherein  $\text{R}^1$  is  $\text{C}_{10}$ - $\text{C}_{18}$  hydrocarbyl and mixtures thereof, preferably  $\text{C}_{10}$ ,  $\text{C}_{12}$ ,  $\text{C}_{14}$  alkyl and mixtures thereof. X is any convenient anion to provide charge balance, preferably chloride.

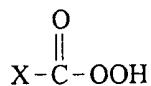
#### 5 Bleach Activator

The detergent compositions of the invention preferably comprise a bleach activator, preferably comprising an organic peroxyacid bleach precursor. It may be preferred that the composition comprises at least two peroxy acid bleach precursors, preferably at least one hydrophobic peroxyacid bleach precursor and at least one  
 10 hydrophilic peroxy acid bleach precursor, as defined herein. The production of the organic peroxyacid occurs then by an in situ reaction of the precursor with a source of hydrogen peroxide. The bleach activator may alternatively, or in addition comprise a preformed peroxy acid bleach. Preferably, the bleach activator is present as a separate, admixed particle.

15 Preferably, any bleach activator is present in a particulate component having an average particle size, by weight, of from 600 microns to 1400 microns, preferably from 700 microns to 1100 microns. It may be preferred that at least 80%, preferably at least 90% or even at least 95 % or even substantially 100% of the component or components comprising the bleach activator have a particle size of from 300 microns to 1700 microns,  
 20 preferably from 425 microns to 1400 microns. Preferred hydrophobic peroxy acid bleach precursor preferably comprise a compound having an oxy-benzene sulphonate group, preferably NOBS, DOBS, LOBS and/ or NACA-OBS. Preferred hydrophilic peroxy acid bleach precursors preferably comprises TAED.

#### Peroxyacid Bleach Precursor

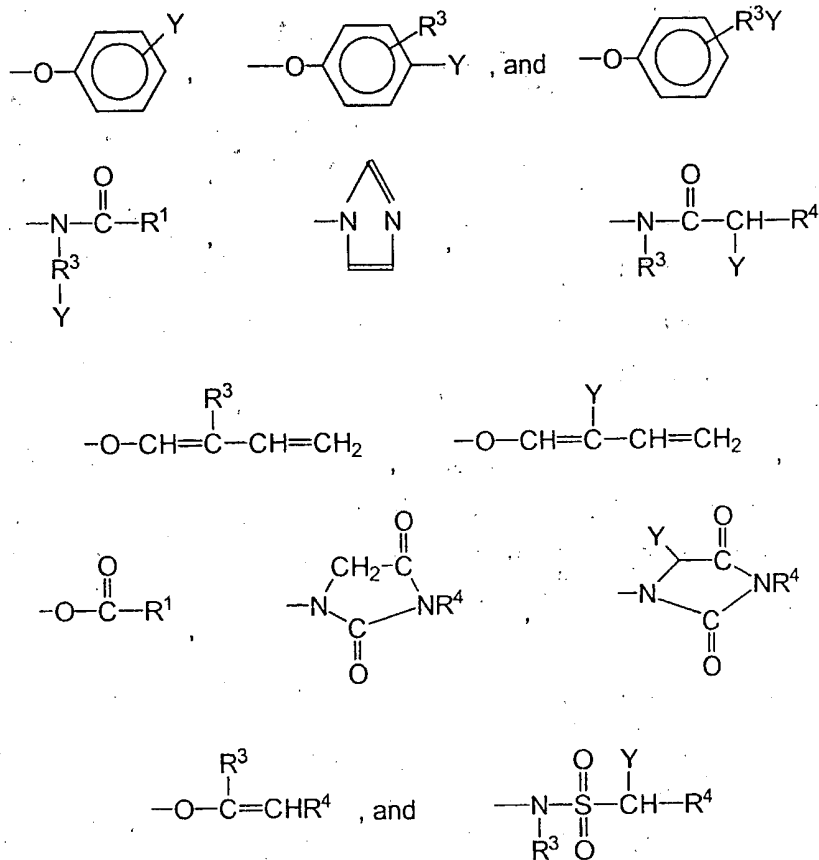
25 Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as  $\text{X-C(O)-L}$  where L is a leaving group and X is essentially any functionality, such that on perhydroloysis the structure of the peroxyacid produced is



For the purpose of the invention, hydrophobic peroxyacid bleach precursors produce a peroxy acid of the formula above wherein X is a group comprising at least 6 carbon atoms and a hydrophilic peroxyacid bleach precursor produces a peroxyacid

- 5 bleach of the formula above wherein X is a group comprising 1 to 5 carbon atoms. The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from the group consisting of:



- and mixtures thereof, wherein  $\text{R}^1$  is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms,  $\text{R}^3$  is an alkyl chain containing from 1 to 8 carbon atoms,  $\text{R}^4$  is H or

$R^3$ , and Y is H or a solubilizing group. Any of  $R^1$ ,  $R^3$  and  $R^4$  may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups.

The preferred solubilizing groups are  $-\text{SO}_3^- \text{M}^+$ ,  $-\text{CO}_2^- \text{M}^+$ ,  $-\text{SO}_4^- \text{M}^+$ ,  $-\text{N}^+(\text{R}^3)_4 \text{X}^-$

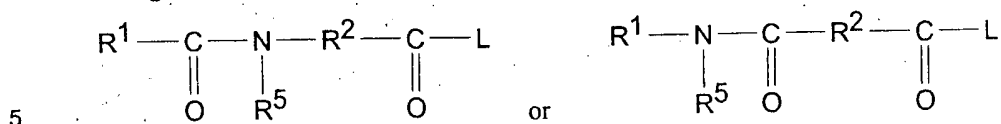
- 5 and  $\text{O}=\text{N}(\text{R}^3)_3$  and most preferably  $-\text{SO}_3^- \text{M}^+$  and  $-\text{CO}_2^- \text{M}^+$  wherein  $\text{R}^3$  is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate  
10 or acetate anion.

- Peroxyacid bleach precursor compounds are preferably incorporated in final detergent compositions at a level of from 0.5% to 30% by weight, more preferably from 1% to 15% by weight, most preferably from 1.5% to 10% by weight. The ratio of hydrophilic to hydrophobic bleach precursors, when present, is preferably from 10:1 to  
15 1:10, more preferably from 5:1 to 1:5 or even from 3:1 to 1:3. Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789.  
20 Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

- Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis. Preferred alkyl percarboxylic precursor compounds of the imide type include the N-  
25 ,N,N<sup>1</sup>N<sup>1</sup> tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred as hydrophilic peroxy acid bleach precursor. Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS);

sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and pentaacetyl glucose.

Amide substituted alkyl peroxyacid precursor compounds are suitable herein, including those of the following general formulae:



wherein  $\text{R}^1$  is an aryl or alkaryl group with from about 1 to about 14 carbon atoms,  $\text{R}^2$  is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and  $\text{R}^5$  is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group.  $\text{R}^1$  preferably contains from about 6 to 12 carbon atoms.  $\text{R}^2$  preferably contains from about 4 to 8 carbon atoms.  $\text{R}^1$  may be straight chain or branched alkyl, substituted aryl or alkaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for  $\text{R}^2$ .  $\text{R}^2$  can include alkyl, aryl, wherein said  $\text{R}^2$  may also contain halogen, nitrogen, sulphur and other typical substituent groups or organic compounds.  $\text{R}^5$  is preferably H or methyl.  $\text{R}^1$  and  $\text{R}^5$  should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386. It can be preferred that  $\text{R}^1$  and  $\text{R}^5$  forms together with the nitrogen and carbon atom a ring structure.

Preferred examples of bleach precursors of this type include amide substituted peroxyacid precursor compounds selected from (6-octanamido-caproyl)oxybenzenesulfonate, (6-decanamido-caproyl) oxybenzene- sulfonate, and the highly preferred (6-nonanamidocaproyl)oxy benzene sulfonate, and mixtures thereof as described in EP-A-0170386.

Perbenzoic acid precursor compounds which provide perbenzoic acid on perhydrolysis benzoxazin organic peroxyacid precursors, as disclosed for example in EP-A-332294 and EP-A-482807 and cationic peroxyacid precursor compounds which produce cationic peroxyacids on perhydrolysis are also suitable.

Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K.

1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332. Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

5            Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams and the trialkyl ammonium methylene alkyl caprolactams.

10           The particles or compositions of the present invention may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid, typically at a level of from 0.1% to 15% by weight, more preferably from 1% to 10% by weight. A preferred class of organic peroxyacid compounds are the amide substituted compounds as described in EP-A-0170386. Other organic peroxyacids  
15 include diacyl and tetraacylperoxides, especially diperoxydodecanedioic acid, diperoxytetradecanedioic acid and diperoxyhexadecanedioic acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also suitable herein.

#### Peroxide Source

20           Inorganic perhydrate salts are a preferred source of peroxide. Preferably these salts are present at a level of from 0.01% to 50% by weight, more preferably of from 0.5% to 30% by weight of the composition.

             Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. Generally these materials are prepared by  
25 crystallisation or fluidised bed processes. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product. Suitable  
30 coatings comprise inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as waxes, oils, or fatty soaps. Sodium perborate is a preferred perhydrate salt and can be in the form of the monohydrate of

- nominal formula  $\text{NaBO}_2\text{H}_2\text{O}_2$  or the tetrahydrate  $\text{NaBO}_2\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ . Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates herein. Sodium percarbonate is an addition compound having a formula corresponding to  $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ , and is available commercially as a crystalline solid. Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

#### Chelants

- As used herein, chelants refers to detergent ingredients which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper. Chelants are generally present in the detergent matrix component and/or as dry added additional detergent ingredients so that they are present in the final detergent composition at total levels of from 0.005% to 10%, preferably from 0.1% to 5%, more preferably from 0.25% to 7.5% and most preferably from 0.3% to 2% by weight of the compositions or component.

- Suitable chelants include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates, preferably, diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate, 1,1 hydroxyethane diphosphonic acid and 1,1 hydroxyethane dimethylene phosphonic acid.

- Other suitable chelants for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof, and iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The  $\beta$ -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable. EP-A-476,257 describes suitable amino



based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N,N'-diglutamic acid (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS) are also suitable. Especially preferred are diethylenetriamine pentacetic acid, ethylenediamine-N,N'-disuccinic acid (EDDS) and 1,1 hydroxyethane diphosphonic acid or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. In particular the chelating agents comprising an amino or amine group can be bleach-sensitive and are suitable in the compositions of the invention.

#### Water-Soluble Builder Compound

The detergent compositions herein preferably contain a water-soluble builder compound, typically present in the detergent compositions at a level of from 1% to 80% by weight, preferably from 10% to 60%, most preferably from 15% to 40% by weight.

One preferred detergent composition of the invention comprises phosphate-containing builder material, preferably present at a level of from 0.5% to 60%, more preferably from 5% to 50%, more preferably from 8% to 40% by weight. Suitable examples of water-soluble phosphate builders are the alkali metal triphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid. The phosphate-containing builder material preferably comprises tetrasodium pyrophosphate or even more preferably anhydrous sodium triphosphate.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, borates, and mixtures of any of the foregoing. The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance. Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of

succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates or their acids containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as  
5 succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447. The most preferred polycarboxylic acid containing three  
10 carboxy groups is citric acid, preferably present at a level of from 0.1% to 15%, more preferably from 0.5% to 8% by weight.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates  
15 containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are hydroxy-carboxylates containing up to three carboxy groups per molecule, particularly citrates.

20 The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components. Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

25 Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 1000-5000 and their copolymers with  
30 maleic anhydride, such copolymers having a molecular weight of from 2000 to 100,000, especially 40,000 to 80,000. The polyamino compounds are also useful herein including

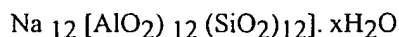
those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

#### Partially Soluble or Insoluble Builder Compound

The compositions of the invention may contain a partially soluble or insoluble  
 5 builder compound present in the detergent matrix component and/or the optional additional ingredients. Where present, typically they will be present in the detergent compositions in a total amount of from 0.5% to 60% by weight, preferably from 5% to 50% by weight, most preferably from 8% to 40% weight. Examples of largely water insoluble builders include the sodium aluminosilicates. As mentioned above, it may be  
 10 preferred in one embodiment of the invention, that only small amounts of aluminosilicate builder are present.

Suitable aluminosilicate zeolites have the unit cell formula  $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$  wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate  
 15 material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X,  
 20 Zeolite HS and mixtures thereof. Zeolite A has the formula:



wherein x is from 20 to 30, especially 27. Zeolite X has the formula  $\text{Na}_{86} [(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$ .

Another preferred aluminosilicate zeolite is zeolite MAP builder. The  
 25 zeolite MAP may be present in amounts from 1 to 80%, more preferably from 15 to 40 wt%. Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, preferably within the range from 0.9 to 1.33 and more preferably within the range of from 0.9 to 1.2. Of particular interest is zeolite  
 30 MAP having a silicon to aluminium ratio not greater than 1.15 and, more particularly, not greater than 1.07. In a preferred aspect the zeolite MAP detergent

builder has a particle size, expressed as a median particle size  $d_{50}$  value of from 1.0 to 10.0 micrometres, more preferably from 2.0 to 7.0 micrometres, most preferably from 2.5 to 5.0 micrometres. The  $d_{50}$  value indicates that 50% by weight of the particles have a diameter smaller than that figure. The particle size may, in particular be determined by conventional analytical techniques such as microscopic determination using a scanning electron microscope or by means of a laser granulometer, described herein. Other methods of establishing  $d_{50}$  values are disclosed in EP 384070A.

Dyes, Perfumes, Enzymes, Optical Brighteners

10 A preferred ingredient of the compositions herein are dyes and dyed particles or speckles, which can be bleach-sensitive. The dye as used herein can be a dye stuff or an aqueous or nonaqueous solution of a dye stuff. It may be preferred that the dye is an aqueous solution comprising a dyestuff, at any level to obtain suitable dyeing of the detergent particles or speckles, preferably such that levels of dye solution are obtained up to 2% by weight of the dyed particle, or more preferably up to 0.5% by weight, as described above. The dye may also be mixed with a non-aqueous carrier material, such as non-aqueous liquid materials including nonionic surfactants. Optionally, the dye also comprising other ingredients such as organic binder materials, which may also be a non-aqueous liquid. The dyestuff can be any suitable dyestuff. Specific examples of suitable dyestuffs include E104 - food yellow 13 (quinoline yellow), E110 - food yellow 3 (sunset yellow FCF), E131 - food blue 5 (patent blue V), Ultra Marine blue (trade name), E133 - food blue 2 (brilliant blue FCF), E140 - natural green 3 (chlorophyll and chlorophyllins), E141 and Pigment green 7 (chlorinated Cu phthalocyanine). Preferred dyestuffs may be Monastral Blue BV paste (trade name) and/ or Pigmasol Green (trade name).

25 Another preferred ingredient of the compositions of the invention is a perfume or perfume composition. Any perfume composition can be used herein. The perfumes may also be encapsulated. Preferred perfumes containing at least one component with a low molecular weight volatile component, e.g. having a molecular weight of from 150 to 450 or preferably 350. Preferably, the perfume component comprises an oxygen-containing functional group. Preferred functional groups are aldehyde, ketone, alcohol or ether functional groups or mixtures thereof.

Another highly preferred ingredient useful in the particles or compositions herein is one or more additional enzymes. Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, cellulases, endolases, esterases, pectinases, lactases and peroxidases conventionally  
5 incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition. Preferred amylases include, for example,  $\alpha$ -amylases described in more detail in GB-1,269,839 (Novo). Preferred commercially  
10 available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl, Duramyl and BAN by Novo Industries A/S. Highly preferred amylase enzymes maybe those described in PCT/US 9703635, and in WO95/26397 and WO96/23873. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from  
20 0.0001% to 2% active enzyme by weight. Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight. The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas  
25 pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272. Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described  
30 in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

The compositions herein also preferably contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners, as mentioned above. Examples are Tinopal-UNPA-GX™ and Tinopal-CBS-X™ by Ciba-Geigy Corporation. Others include Tinopal 5BM-GX™, Tinopal-DMS-X™ and Tinopal AMS-GX™ by Ciba Geigy Corporation.

#### Photo-Bleaching Agent

Photo-bleaching agents are preferred ingredients of the compositions or components herein. Preferred photo-bleaching agent herein comprise a compounds having a porphin or porphyrin structure. Porphin and porphyrin, in the literature, are used as synonyms, but conventionally porphin stands for the simplest porphyrin without any substituents; wherein porphyrin is a sub-class of porphin. The references to porphin in this application will include porphyrin. The porphin structures preferably comprise a metal element or cation, preferably Ca, Mg, P, Ti, Cr, Zr, In, Sn or Hf, more preferably Ge, Si or Ga, or more preferably Al, most preferably Zn. It can be preferred that the photo-bleaching compound or component is substituted with substituents selected from alkyl groups such as methyl, ethyl, propyl, t-butyl group and aromatic ring systems such as pyridyl, pyridyl-N-oxide, phenyl, naphthyl and anthracyl moieties. The photo-bleaching compound or component can have solubilizing groups as substituents. Alternatively, or in addition hereto the photo-bleaching agent can comprise a polymeric component capable of solubilizing the photo-bleaching compound, for example PVP, PVNP, PVI or copolymers thereof or mixtures thereof. Highly preferred photo-bleaching compounds are compounds having a phthalocyanine structure, which preferably have the metal elements or cations described above.

The phthalocyanines can be substituted for example the phthalocyanine structures which are substituted at one or more of the 1-4, 6, 8-11, 13, 15-18, 20, 22-25, 27 atom positions.

#### Organic Polymeric Ingredients

Organic polymeric compounds are preferred additional herein and are preferably present as components of any particulate component such as the detergent matrix component where they may act as binders. By organic polymeric compound it is meant herein essentially any polymeric organic compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions, including any of:

the high molecular weight organic polymeric compounds described as clay flocculating agents herein, including quaternised ethoxylated (poly) amine clay-soil removal/ anti-redeposition agent in accord with the invention. Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from

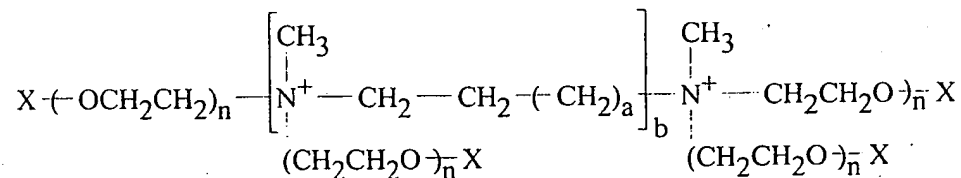
5 0.01% to 30%, preferably from 0.1% to 15%, most preferably from 0.5% to 10% by weight of the compositions or component. Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein. Other organic polymeric compounds suitable for incorporation in the detergent

10 compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. Highly preferred polymeric components herein are cotton

15 and non-cotton soil release polymer according to U.S. Patent 4,968,451, Scheibel et al., and U.S. Patent 5,415,807, Gosselink et al., and in particular according to US application no.60/051517. Another organic compound, which is a preferred clay dispersant/ anti-redeposition agent, for use herein, can be the ethoxylated cationic monoamines and diamines of the formula:

20



wherein X is a nonionic group selected from the group consisting of H, C<sub>1</sub>-C<sub>4</sub> alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof, a is from 0 to 20, preferably from 0 to 4 (e.g. ethylene, propylene, hexamethylene) b is 1 or 0; for cationic

25 monoamines (b=0), n is at least 16, with a typical range of from 20 to 35; for cationic diamines (b=1), n is at least about 12 with a typical range of from about 12 to about 42. Other dispersants/ anti-redeposition agents for use herein are described in EP-B-011965 and US 4,659,802 and US 4,664,848.

Polymeric dye transfer inhibiting agents when present are generally in amounts from 0.01% to 10 %, preferably from 0.05% to 0.5% and are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof, whereby these polymers can be cross-linked polymers.

Polymeric soil release agents, hereinafter "SRA", can optionally be employed in the present components or compositions. If utilized, SRAs will generally be used in amounts from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight. Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles, thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the SRA to be more easily cleaned in later washing procedures. Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without, of course, forming a densely crosslinked overall structure.

Suitable SRAs are for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Other SRAs include the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al. Other examples of SRA's include: the partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al. SRAs also include: simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; the C<sub>1</sub>-C<sub>4</sub> alkyl celluloses and C<sub>4</sub> hydroxyalkyl celluloses, see U.S. 4,000,093, December 28, 1976



to Nicol, et al.; and the methyl cellulose ethers having an average degree of substitution (methyl) per anhydroglucose unit from about 1.6 to about 2.3 and a solution viscosity of from about 80 to about 120 centipoise measured at 20°C as a 2% aqueous solution. Such materials are available as METOLOSE SM100 and METOLOSE SM200, which are the  
5 trade names of methyl cellulose ethers manufactured by Shin-etsu Kagaku Kogyo KK.

Additional classes of SRAs include those described in U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al.; U.S. 4,525,524 Tung et al., and U.S. 4,201,824, Violland et al.

#### Suds Suppressing System

10 The detergent compositions herein, in particular when formulated for use in machine washing compositions, may comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.02% to 10%, most preferably from 0.05% to 3% by weight of the composition or component. Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for  
15 example silicone antifoam compounds and 2-alkyl alcanol antifoam compounds or soap. By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam  
20 compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes,  
25 particularly the polydimethylsiloxanes having trimethylsilyl end blocking units. Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof as described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols,  
30 aliphatic C<sub>18</sub>-C<sub>40</sub> ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyl diamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1

to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

A preferred suds suppressing system comprises antifoam compound, preferably comprising in combination polydimethyl siloxane, at a level of from 50% to 99%,  
5 preferably 75% to 95% by weight of the silicone antifoam compound; and silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content  
10 of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10% such as DCO544, commercially available from DOW Corning, and an inert carrier fluid compound, most preferably comprising a C<sub>16</sub>-C<sub>18</sub> ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of 5 to 80%, preferably 10 to 70% by weight.

15 A highly preferred particulate suds suppressing system is described in EP-A-0210731. EP-A-0210721 discloses other preferred particulate suds suppressing systems.

Other highly preferred suds suppressing systems comprise polydimethylsiloxane or mixtures of silicone, such as polydimethylsiloxane, aluminosilicate and polycarboxylic polymers, such as copolymers of laic and acrylic acid.

20 Other optional ingredients suitable for inclusion in the compositions of the invention include colours and filler salts, with sodium sulfate being a preferred filler salt.

Highly preferred compositions contain from about 2% to about 10% by weight of an organic acid, preferably citric acid. Also, preferably combined with a carbonate salt, minor amounts (e.g., less than about 20% by weight) of neutralizing agents, buffering  
25 agents, phase regulants, hydrotropes, enzyme stabilizing agents, polyacids, suds regulants, opacifiers, anti-oxidants, bactericides and dyes, such as those described in US Patent 4,285,841 to Barrat et al., issued August 25, 1981 (herein incorporated by reference), can be present.

The detergent compositions can include as an additional component a chlorine-  
30 based bleach. However, since the detergent compositions of the invention are solid, most liquid chlorine-based bleaching will not be suitable for these detergent compositions and only granular or powder chlorine-based bleaches will be suitable. Alternatively, a

chlorine based bleach can be added to the detergent composition by the user at the beginning or during the washing process. The chlorine-based bleach is such that a hypochlorite species is formed in aqueous solution. The hypochlorite ion is chemically represented by the formula  $\text{OCI}^-$ . Those bleaching agents which yield a hypochlorite species in aqueous solution include alkali metal and alkaline earth metal hypochlorites, hypochlorite addition products, chloramines, chlorimines, chloramides, and chlorimides. Specific examples include sodium hypochlorite, potassium hypochlorite, monobasic calcium hypochlorite, dibasic magnesium hypochlorite, chlorinated trisodium phosphate dodecahydrate, potassium dichloroisocyanurate, sodium dichloroisocyanurate sodium dichloroisocyanurate dihydrate, trichlorocyanuric acid, 1,3-dichloro-5,5-dimethylhydantoin, N-chlorosulfamide, Chloramine T, Dichloramine T, chloramine B and Dichloramine B. A preferred bleaching agent for use in the compositions of the instant invention is sodium hypochlorite, potassium hypochlorite, or a mixture thereof. A preferred chlorine-based bleach can be Triclosan (trade name).

Most of the above-described hypochlorite-yielding bleaching agents are available in solid or concentrated form and are dissolved in water during preparation of the compositions of the instant invention. Some of the above materials are available as aqueous solutions.

#### Laundry Washing Method

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. By an effective amount of the detergent composition it is meant from 10g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods. Preferred washing machines may be the so-called low-fill machines.

In a preferred use aspect the composition is formulated such that it is suitable for hard-surface cleaning or hand washing. In another preferred aspect the detergent composition is a pre-treatment or soaking composition, to be used to pre-treat or soak soiled and stained fabrics.

#### EXAMPLES

The following examples are presented for illustrative purposes only and are not to be construed as limiting the scope of the appended claims in any way.

**Abbreviations used in the Examples**

In the detergent compositions, the abbreviated component identifications have the

5 following meanings:

- |    |             |   |
|----|-------------|---|
|    | LAS         | : Sodium linear C11-13 alkyl benzene sulfonate  |
|    | TAS         | : Sodium tallow alkyl sulfate   |
|    | CxyAS       | : Sodium C1x - C1y alkyl sulfate  |
|    | Branched AS | : branched sodium alkyl sulfate as described in WO99/19454  |
| 10 | C46SAS      | : Sodium C14 - C16 secondary (2,3) alkyl sulfate  |
|    | CxyEzS      | : Sodium C1x-C1y alkyl sulfate condensed with z moles of ethylene oxide   |
|    | CxyEz       | : C1x-C1y predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide   |
|    | QAS         | : $R_2.N+(CH_3)_2(C_2H_4OH)$ with $R_2 = C_{12} - C_{14}$   |
| 15 | QAS 1       | : $R_2.N+(CH_3)_2(C_2H_4OH)$ with $R_2 = C_8 - C_{11}$  |
|    | APA         | : C8 - C10 amido propyl dimethyl amine  |
|    | Soap        | : Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut fatty acids   |
|    | STS         | : Sodium toluene sulphonate   |
| 20 | CFAA        | : C12-C14 (coco) alkyl N-methyl glucamide   |
|    | TFAA        | : C16-C18 alkyl N-methyl glucamide  |
|    | TPKFA       | : C12-C14 topped whole cut fatty acids  |
|    | STPP        | : Anhydrous sodium tripolyphosphate   |
|    | TSPP        | : Tetrasodium pyrophosphate   |
| 25 | Zeolite A   | : Hydrated sodium aluminosilicate of formula $Na_{12}(Al_2Si_2O_7)_{12} \cdot 27H_2O$ having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis) |
|    | NaSKS-6     | : Crystalline layered silicate of formula d- $Na_2Si_2O_5$  |
|    | Citric acid | : Anhydrous citric acid   |
| 30 | Borate      | : Sodium borate   |
|    | Carbonate   | : Anhydrous sodium carbonate: particle size 200 $\mu$ m to 900 $\mu$ m  |

	Bicarbonate	:Anhydrous sodium bicarbonate with a particle size distribution between 400µm and 1200µm
	Silicate	:Amorphous sodium silicate (SiO <sub>2</sub> :Na <sub>2</sub> O = 2.0:1)
	Sulfate	:Anhydrous sodium sulfate
5	Mg sulfate	:Anhydrous magnesium sulfate
	Citrate	:Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425µm and 850µm
	MA/AA	:Copolymer of 1:4 maleic/acrylic acid, average m. wt. about 70,000
	MA/AA (1)	:Copolymer of 4:6 maleic/acrylic acid, average m. wt. about 10,000
10	AA	:Sodium polyacrylate polymer of average molecular weight 4,500
	CMC	:Sodium carboxymethyl cellulose
	Cellulose ether	:Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals
	Protease	:Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by
15		NOVO Industries A/S under the tradename Savinase
	Protease I	:Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc.
	Alcalase	:Proteolytic enzyme, having 5.3% by weight of active enzyme, sold by
		NOVO Industries A/S
20	Cellulase	:Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by
		NOVO Industries A/S under the tradename Carezyme
	Amylase	:Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by
		NOVO Industries A/S under the tradename Termamyl 120T
	Lipase	:Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by
25		NOVO Industries A/S under the tradename Lipolase
	Lipase (1)	:Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by
		NOVO Industries A/S under the tradename Lipolase Ultra
	Endolase	:Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by
		NOVO Industries A/S
30	PB4	:Sodium perborate tetrahydrate of nominal formula NaBO <sub>2</sub> .3H <sub>2</sub> O.H <sub>2</sub> O <sub>2</sub> -
	PB1	:Anhydrous sodium perborate bleach of nominal formula NaBO <sub>2</sub> .H <sub>2</sub> O <sub>2</sub>
	Percarbonate	:Sodium percarbonate of nominal formula 2Na <sub>2</sub> CO <sub>3</sub> .3H <sub>2</sub> O <sub>2</sub>

- NOBS :Nonanoyloxybenzene sulfonate in the form of the sodium salt
- NAC-OBS :(6-nonamidocaproyl) oxybenzene sulfonate
- TAED :Tetraacetylenediamine
- DTPA :Diethylene triamine pentaacetic acid
- 5 DTPMP :Diethylene triamine penta (methylene phosphonate), marketed by  
Monsanto under the Tradename Dequest 2060
- EDDS :Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer sodium salt.
- Photoactivated  
bleach :Sulfonated zinc phthlocyanine encapsulated in bleach (1) dextrin- sol.pol.
- 10 Photoactivated  
bleach :Sulfonated alumino phthlocyanine encapsulated in bleach (2) dextrin  
soluble polymer
- Brightener 1 :Disodium 4,4'-bis(2-sulphostyryl)biphenyl
- Brightener 2 :Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino)
- 15 stilbene-2:2'-disulfonate
- HEDP :1,1-hydroxyethane diphosphonic acid
- PEGx :Polyethylene glycol, with a molecular weight of x (typically 4,000)
- PEO :Polyethylene oxide, with an average molecular weight of 50,000
- TEPAE :Tetraethylenepentaamine ethoxylate
- 20 PVI :Polyvinyl imidosole, with an average molecular weight of 20,000
- PVP :Polyvinylpyrrolidone polymer, with an average m. wt. of 60,000
- PVNO :Polyvinylpyridine N-oxide polymer, with an av. m. wt. of 50,000
- PVPVI :Copol of polyvinylpyrrolidone and vinylimidazole (av. m wt of 20,000)
- QEA :bis((C<sub>2</sub>H<sub>5</sub>O)(C<sub>2</sub>H<sub>4</sub>O)<sub>n</sub>)(CH<sub>3</sub>) -N+-C<sub>6</sub>H<sub>12</sub>-N+-(CH<sub>3</sub>) bis((C<sub>2</sub>H<sub>5</sub>O)-  
25 (C<sub>2</sub>H<sub>4</sub> O)<sub>n</sub>), wherein n = from 20 to 30
- SRP 1 :Anionically end capped poly esters
- SRP 2 :Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
- PEI :Polyethyleneimine with an average molecular weight of 1800 and an  
average ethoxylation degree of 7 ethyleneoxy residues per nitrogen
- 30 Silicone antifoam :Polydimethylsiloxane foam controller with siloxane-oxyalkylene  
copolymer as dispersing agent with a ratio of said foam controller  
to said dispersing agent of 10:1 to 100:1

Opacifier :Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621

Wax :Paraffin wax

HMEO :Hexamethylenediamine tetra(ethylene oxide)24

5 Example 1: Preparation of Effervescence Particle

A 2 kg batch of citric acid and sodium carbonate having a composition of 64wt% citric acid/36 wt% sodium carbonate was prepared by mixing in a Hosokawa Mikron 'Nautamix' DBY-5R rotating screw mixer for five minutes at a speed setting of 9(maximum): 1280 g anhydrous citric acid ex Citrique Belge (Fine Granular Grade: 10 16/40) having a particle size of from 200-400 $\mu$ m and 720g anhydrous Sodium Carbonate(Light Soda Ash ex Brunner Mond) pre-milled using a Hosokawa Mikron Air-Classifying Mill(ACM 15) to a median particle size of 5 $\mu$ m. The mixture was then compacted in a Bepex Compaction Unit (Roll 200mm Diameter, 50mm Width): the pre-mixed powders were poured into the feed-hopper above the compacting rolls. The feed- 15 hopper has a vertical screw which feeds the powder into the rolls. The force applied to push these two rolls together known as compaction force was adjusted to 80kN by adjusting the feed-screw speed. The compacted material was collected in the form of broken and unbroken corrugated sheets which were then milled in a Hosokawa Bepex F200 Flake Breaker at speed setting 1. This equipment consists of a Rolling Cage with a 20 1000 $\mu$ m Screen.

The material produced by the Flake breaker was then placed on a Vibrating Sieving device( Retsch model AST200) with sieve size of 355 $\mu$ m. The material retained on the screen was the desired finished particle (effervescence particle A in the table below) with median particle size 620 $\mu$ m, and the fines were removed for recycle.

25 The process is repeated using the following mixtures of components in the quantities (respective amounts are given in wt% based on the effervescence particle) given in table 1, to make alternative effervescence particles B-E.

Table 1

Effervescence Particle	B	C	D	E
Citric acid	40	10	55	-

Malic acid	20	30	-	35
Tartaric acid	-	-	-	15
Sodium carbonate	25	70	-	40
Sodium bicarbonate	15	-	45	10

These effervescence particles are then incorporated into detergent compositions as set out in Examples 2 to 6.

#### 5 Example 2

A spray dried granule, having the composition set out in example 3 below, produced by forming an aqueous slurry which is then formed into particulates in a spray-drying tower is then mixed with, 5 wt% TAED, 1 wt% suds suppressor, 7.5 wt% sodium carbonate and 2.5 wt% sodium sulphate, as additional detergent ingredients in an Eirich mixer. An aqueous solution of PEG-4000 (35% by weight solids) is then sprayed onto the mixture, which is allowed to granulate for 5 minutes. The resultant product is screened to collect particles between 300 and 1200 microns. 10 wt% sodium percarbonate, 0.5 wt% perfume and 1 wt% enzymes (comprising a mixture of prills comprising amylase, cellulase, protease and lipase) are then dry added and mixed. The mixture produced has an eRH of 59%. 10 wt% effervescence particles of any of formulations A to E or mixtures of these are then added to this mixture in a Nautamix conical mixer and subsequently packed into detergent cartons.

#### Example 3

20 A spray dried granule is produced on a counter-current spray drying tower with an air inlet temperature of 300°C. Agglomerates and other admixes (see Table 2) are mixed with the spray dried granule in a batch rotating drum mixer. The detergent matrix has an eRH of 38%. The effervescence particle A is then added, and the product is then packed into detergent cartons. Further examples of detergent compositions according to the invention may be prepared by the use of effervescence particles B to E or mixtures of any of the particles A to E.



Table 2

<u>Spray dried Granule</u>		50%	
	Spray dried granule composition		% Weight of Total
5	Feed		
	LAS		10.4
	Tallow Alkyl Sulphate		1.6
	EDDS		0.4
	Brightener 15		0.1
10	Magnesium sulphate		0.7
	Sokalan CP5		2.5
	HEDP		0.3
	Sodium carbonate		8.4
	Sodium sulphate		23.5
15	Zeolite A		40.0
	Misc. (water, perfume, etc.)		<u>12.07</u>
			100.0
<u>Anionic surfactant agglomerate</u>		10%	
20	Agglomerate composition		% Weight of Total
	Feed		
	C <sub>45</sub> alkyl ethoxylate sulfate (EO 0.6)		29.1
	Zeolite A		45.0
	Sodium carbonate		15.1
25	Polyethylene glycol (MW 4000)		1.3
	Misc. (water, perfume, etc.)		<u>9.5</u>
			100.0
	<u>Percarbonate</u>	<u>10%</u>	
	<u>TAED</u>	<u>5%</u>	
30	<u>Effervescence granule</u>	<u>10%</u>	
	<u>Minors</u>	<u>15%</u>	

Example 4

Example 3 is repeated except that the spray dried granule is dried at the higher tower inlet temperature of 350°C and some of the bound moisture is removed. In this case the detergent matrix eRH was 24%.

5 Example 5

The detergent matrix of example 3 is reproduced and to it is added 5% of overdried zeolite in a Nautamix conical mixer. (Overdried zeolite is a Zeolite A which has had more than half of the water of crystallisation removed by additional drying). The resulting detergent matrix has an eRH of 12%. 10% of effervesence particle B is then added to this  
10 matrix and the product packed into detergent cartons. Alternative examples can be prepared by the use of any of effervesence particles B to E or mixtures of any of particles A to E.

Example 6

Spray dried particles, agglomerates and builder agglomerates of the formulation  
15 described in Tables 3A and 3B below are fed first into a Lodige KM™ 600 mixer at 660 kg, with the drum rotation at 100 RPM and cutter speed at 3600RPM. The resulting mixture is fed into a fluid bed dryer. Optionally an aqueous solution of PEG-4000 (30% by weight solids) is sprayed onto the mixture in the first of three stages in the fluid bed dryer. The resulting product is screened to collect the particles in the range of about 600  
20 to about 1100µ. The fines are recycled to the Lodige KM and the large particles are ground and recycled to the fluid bed dryer. The dry-add detergent components and spray-on from the tables below are then added. The detergent matrix eRH was typically around 14%.

25

**TABLE 3 A**

The following compositions are in accordance with the invention.

	A	B	C	D	E	F	G	H	I
<u>Spray-dried Granules</u>									
LAS	10.0	10.0	15.0	5.0	8.0	10.0	-	-	-
TAS	-	1.0	-	-	-	-	-	-	-

MBAS	-	-	-	5.0	8.0	-	-	-
C <sub>45</sub> AS	-	-	1.0	-	1.0	2.0	-	-
C <sub>45</sub> AE <sub>3</sub> S	-	-	-	1.0	-	-	-	-
QAS	-	-	1.0	1.0	-	-	-	-
DTPA, HEDP and/or EDDS	0.3	0.3	0.5	0.3	-	-	-	-
MgSO <sub>4</sub>	0.5	0.5	0.1	-	-	-	-	-
Sodium citrate	-	-	-	3.0	5.0	-	-	-
Sodium carbonate	10.0	7.0	15.0	-	10.0	10.0	-	-
Sodium sulphate	5.0	5.0	-	-	5.0	3.0	-	-
Sodium silicate 1.6R	-	-	-	-	2.0	-	-	-
Zeolite A	16.0	18.0	20.0	20.0	-	-	-	-
SKS-6	-	-	-	3.0	5.0	-	-	-
MA/AA or AA	1.0	2.0	11.0	-	-	2.0	-	-
PEG 4000	-	2.0	-	1.0	-	1.0	-	-
QEA	1.0	-	-	-	1.0	-	-	-
Brightener	0.05	0.05	0.05	-	0.05	-	-	-
Silicone oil	0.01	0.01	0.01	-	-	0.01	-	-
<u>Agglomerate</u>								
LAS	-	-	-	-	-	-	2.0	2.0
MBAS	-	-	-	-	-	-	-	1.0
C <sub>45</sub> AS	-	-	-	-	-	-	2.0	-
AE <sub>3</sub>	-	-	-	-	-	-	-	1.0
Carbonate	-	-	-	-	-	1.0	1.0	1.0
Sodium citrate	-	-	-	-	-	-	-	5.0
CFAA	-	-	-	-	-	-	-	-
Citric acid	-	-	-	-	-	4.0	-	1.0
QEA	-	-	-	-	-	2.0	2.0	1.0
SRP	-	-	-	-	-	1.0	1.0	0.2

Zeolite A						15.0	26.0	15.0	16.0
Sodium silicate									
PEG							4.0		
<u>Builder Agglomerates</u>									
SKS-6	6.0				6.0	3.0		7.0	10.0
LAS	4.0	5.0			5.0	3.0		10.0	12.0
<u>Dry-add particulate components</u>									
Effervescence Particle A	8.0	10.0			12.0			2.0	4.0
Effervescence Particle B			10.0						
Effervescence Particle C				4.0					
Effervescence Particle D						8.0			
Effervescence Particle E							2.0		
QEA				0.2	0.5				
NACAOBS	3.0			1.5				2.5	
NOBS		3.0	3.0						5.0
TAED	2.5			1.5	2.5	6.5		1.5	
MBAS				8.0			8.0		4.0
LAS (flake)	10.0	10.0						8.0	
<u>Spray-on</u>									
Brightener	0.2	0.2	0.3	0.1	0.2	0.1		0.6	
Dye				0.3	0.05	0.1			

AE7	-	-	-	-	-	0.5	-	0.7	-
Perfume	-	-	-	0.8	-	0.5	-	0.5	-
<u>Dry-add</u>									
Citrate	-	-	20.0	4.0	-	5.0	15.0	-	5.0
Percarbonate	15.0	3.0	6.0	10.0	-	-	-	18.0	5.0
Perborate	-	-	-	-	6.0	18.0	-	-	-
Photobleach	0.02	0.02	0.02	0.1	0.05	-	0.3	-	0.03
Enzymes (cellulase, amylase, protease, lipase)	1.3	0.3	0.5	0.5	0.8	2.0	0.5	0.16	0.2
Carbonate	0.0	10.0	-	-	-	5.0	8.0	10.0	5.0
Perfume (encapsulated)	0.6	0.5	0.5	-	0.3	0.5	0.2	0.1	0.6
Suds suppressor	1.0	0.6	0.3	-	0.10	0.5	1.0	0.3	1.2
Soap	0.5	0.2	0.3	3.0	0.5	-	-	0.3	-
Citric acid	-	-	-	6.0	6.0	-	-	-	5.0
Dyed carbonate (blue, green)	0.5	0.5	1.0	2.0	-	0.5	0.5	0.5	1.0
SKS-6	-	-	-	4.0	-	-	-	6.0	-
Fillers up to 100%									

**TABLE 3 B**

The following compositions are in accordance with the invention.

	A	B	C	D	E	F	G	H	I
<u>Spray-Dried Granules</u>									
LAS	10.0	10.0	16.0	5.0	5.0	10.0	-	-	-
TAS	-	1.0	-				-	-	-
MBAS	-	-	-	5.0	5.0		-	-	-
C <sub>45</sub> AS	-	-	1.0		2.0	2.0	-	-	-



PEG	-	-	-	-	-	-	4.0	-	-
<u>Builder Agglomerate</u>									
SKS-6	6.0	5.0	-	-	6.0	3.0	-	7.0	10.0
LAS	4.0	5.0	-	-	5.0	3.0	-	10.0	12.0
<u>Dry-add particulate components</u>									
Effervescence Particle A	8.0		4.0	4.0	-		2.0	2.0	4.0
Effervescence Particle B		10.0							
Effervescence Particle D						8.0			
QEA	-	-	-	0.2	0.5	-	-	-	-
NACAOBS	3.0	-	-	1.5	-	-	-	2.5	-
NOBS	-	3.0	3.0	-	-	-	-	-	5.0
TAED	2.5	-	-	1.5	2.5	6.5	-	1.5	-
MBAS	-	-	-	8.0	-	-	8.0	-	4.0
LAS (flake)	-	-	-	-	-	-	-	8.0	-
<u>Spray-on</u>									
Brightener	0.2	0.2	0.3	0.1	0.2	0.1	-	0.6	-
Dye	-	-	-	0.3	0.05	0.1	-	-	-
AE7	-	-	-	-	-	0.5	-	0.7	-
Perfume	-	-	-	0.8	-	0.5	-	0.5	-
<u>Dry-add</u>									
Citrate	4.0	-	3.0	4.0	-	5.0	15.0	-	5.0
Percarbonate	15.0	3.0	6.0	10.0	-	-	-	18.0	5.0





What is Claimed is:

1. A reactive particle comprising two particulate reactants which react together on contact with a reaction-promoting fluid, in which the particle number ratio of the first reactant to the second reactant (that is the ratio of number of particles of the first reactant to the second reactant) is at least 50:1.
2. A reactive particle according to claim 1 in which the ratio of the median particle size of the second reactant to the first reactant is at least 2:1.
3. A reactive particle according to claim 1 or claim 2 in which the reaction-promoting fluid comprises water either in the gaseous or liquid phase.
4. A reactive particle according to any preceding claim in which the particle is an effervescence particle and at least one of each of the first and second reactants are respectively, an alkaline source and an acid source.
5. A reactive particle according to any preceding claim in which the particle number ratio of the first reactant to the second reactant (that is the ratio of number of particles of the first reactant to the second reactant) is at least 500:1.
6. A reactive particle according to any preceding claim in which the ratio of the median particle size of the second reactant to the first reactant is at least 8:1.
7. A reactive particle according to any preceding claim in which the span of the particle size of each reactant is no greater than 2.
8. A reactive particle according to any preceding claim in which the median particle size of the second reactant is preferably greater than 100 $\mu$ m.
9. A reactive particle according to any preceding claim in which the median particle size of the first reactant is preferably below 50 $\mu$ m.
10. A reactive particle according to any preceding claim which is an effervescence particle and the first reactant comprises the alkali source, and the second reactant comprises the acid source.
11. A reactive particle according to any preceding claim in which the first reactant is present in an amount of from 15% to 70% by weight of the particle.
12. A reactive particle according to any preceding claim in which the second reactant is present in an amount from 35% to 75% by weight of the particle.
13. A reactive particle according to any preceding claim in which one of the first and second reactants comprises citric acid and the second of the first and second reactants

comprises a carbonate-alkali source selected from sodium carbonate and sodium bicarbonate or mixtures thereof.

14. A reactive particle according to any preceding claim comprising an overall moisture content which is less than 0.5 wt% of the effervescence particle.
- 5 15. A detergent composition comprising a reactive particle according to any preceding claim which is an effervescence particle, and a detergent matrix.
16. A detergent composition according to claim 15 in which the detergent matrix has an eRH of no greater than 30%.
17. A method for making a composition according to claim 15 or claim 16 in which the  
10 detergent matrix comprises a detergent matrix component which is firstly prepared by a spray-drying process and then mixed with the reactive particle.
18. A method for making a reactive particle according to any of claims 1 to 17 in which after mixing the first and second reactants are formed into a particle by a pressure agglomeration process.
- 15 19. A method according to claim 18 in which the pressure agglomeration step takes place at a Relative Humidity below 35%.
20. A method according to claim 19 in which the mixing of the first and second reactants also takes place at a Relative Humidity below 35%.
21. A method for washing soiled surfaces, particularly a laundry washing process,  
20 comprising dissolving a detergent composition comprising effervescence particles to form an aqueous solution and contacting the solution with the soiled surfaces for washing.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
3 May 2001 (03.05.2001)

PCT

(10) International Publication Number  
**WO 01/30949 A3**

- (51) International Patent Classification<sup>7</sup>: **C11D 3/04**, 3/10, 3/20
- (21) International Application Number: PCT/US00/29295
- (22) International Filing Date: 23 October 2000 (23.10.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
9925472.4 28 October 1999 (28.10.1999) GB
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- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KR (utility model), KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— with international search report
- (88) Date of publication of the international search report:  
21 February 2002
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



**WO 01/30949 A3**

(54) Title: DETERGENT COMPOSITIONS

(57) Abstract: A detergent composition which dispenses and dissolves well in aqueous solution and having good storage stability is described. The composition comprises a reactive particle which preferably comprises first and second reactants which are respectively, acid and alkali-sources and which release gas on contact with water, in which the particle number ratio of the first reactant to the second reactant (that is the ratio of number of particles of the first reactant to the second reactant) in the reactive particle is at least 50:1. The reactive particles themselves are also claimed.

## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US 00/29295A. CLASSIFICATION OF SUBJECT MATTER  
C11D3/04, C11D3/10, C11D3/20According to International Patent Classification (IPC) or to both national classification and IPC<sup>4</sup>

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2315762 A (THE PROCTER & GAMBLE COMPANY) 11 February 1998, page 4, lines 10-14, page 14, line 15 - page 15, line 3, claims 1,3,4,5.	1, 4, 10, 21
X	FR 2477174 A1 (LICHTENBERG JEAN-PAUL) 04 September 1981, claims.	1, 4, 10, 13, 21
X	FR 2708852 A1 (SALSARULO GILLES) 17 February 1995, abstract, claim 1.	1, 4, 10, 13
X	FR 2708853 A1	1, 4,

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search  
20 December 2000

Date of mailing of the international search report

02.05.01

Name and mailing address of the ISA

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## INTERNATIONAL SEARCH REPORT

International Application No:

- 2 -

PCT/US 00/29295

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 99/12525 A1 (GARRUTO, F.) 18 March 1999, claims. ---	1, 3, 4, 10, 13
X	EP 0752466 A1 (THE PROCTER & GAMBLE COMPANY) 08 January 1997, claims, example. -----	1, 3, 4, 10, 13, 21

<b>ANHANG</b> Zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.	<b>ANNEX</b> To the International Search Report to the international Patent Application No.	<b>ANNEXE</b> Au rapport de recherche international relatif à la demande de brevet international n°	
In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentedokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.	This annex lists the patent family members relating to the patent documents cited in the above-mentioned search report. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.	La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office.	
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